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EFFECT OF ADDING PHOSPHORUS OXIDE ON THE DILATOMETRIC PROPERTIES OF SILICATE CONTAINER GLASSES

S. V. Mulevanov,[1] N. I. Min'ko,[1] and S. A. Kemenov[1]

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It is shown that introducing small amounts of P_2O_5, which do not give rise to opacification and opalescence, into silicate glasses strongly affects the dilatometric properties of glasses. This gives an idea of the structural changes and could be of practical value.

The introduction of small amounts of phosphorus oxide, which do not give rise to opacification and opalescence, into silicate glasses can be used to improve the technological and functional properties. For example, is shown in [1, 2] that adding 0.3%[2] P_2O_5 to the commercial compositions of sheet glass from the vertical drawing system decreases the liquidus temperature by 25 – 50°C and decreases the linear rate of growth of crystals, which makes it possible to increase the drawing rate and improve the quality of the product.

The effect of small additions of P_2O_5 on the properties of container glass with a lower content of magnesium oxide (1.5 – 1.8%) has been investigated in [3]. It was established that replacing 1% SiO_2 by P_2O_5 does not greatly change the high-temperature viscosity, on the basis of which it is asserted that the partial coefficients of P_2O_5 for these properties are equal to the coefficients for SiO_2. The technological advantage of introducing small amounts of P_2O_5 is a decrease of the liquidus temperature (by 15°C), which makes it possible to decrease the founding temperature and to increase the content of the cheaper component (CaO) in the composition. For chemical stability, it is noted that the mass losses in water decrease. The authors attribute this to an increase in the polymerization of the structure. On the whole, the effect of phosphorus oxide on the basic physical-chemical properties of glasses is not unique. It is determined by the concentration of P_2O_5 and the chemical composition of the matrix glass, primarily by the presence of alkali oxides and Al_2O_3 in the glass [4, 5].

Silicophosphate glasses are systems with two glass-forming cations, each of which can form its own characteristic anionic motif. Phosphorus is a stronger cation than silicon (according to the data in [6], the ionic radii of Si and P are 0.039 and 0.035 nm, the energy of the Si – O bond is 443 kJ/mole and the energy of the P – O is 464 kJ/mole, the coordination number of Si and P is 4). For phosphorus, there are stoichiometric differences with silicon (a higher charge of the ion and the presence of the double bond P = O), which could be the reason for their structural incompatibility.

In the opinion of the authors of [7], the introduction of small quantities of P_2O_5 into glassy silica results in a distortion and rupture of the bonds and increases the content of non-bridge oxygen (Fig. 1*a*). For substantial P_2O_5 content (about 44%, molar content), the formation of a single silicon – phosphate framework where the tetrahedra $[P^{5+}O_4]$ have two P – O bonds, equal in length and multiplicity, can form. For high concentrations of phosphorus, judging from the character of the change in the properties of the glasses (density, thermal expansion, index of refraction), hexacoordinated silicon can form.

The structural state of a mixed silicon – phosphate glass-forming framework cannot be stable because of symmetry and excess charge on the tetrahedra $[P^{5+}O_4]$. The structure of the glass is more compensated when Al_2O_3 is present in the composition (Fig. 1*b*).

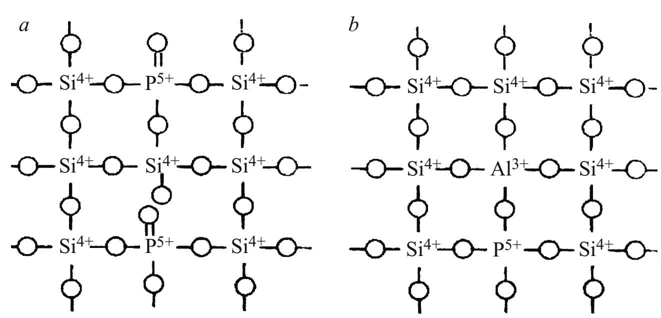

Fig. 1. Fragments of a possible variant of the structure of silicophosphate (*a*) and alumosilicophosphate (*b*) glasses.

[1] V. G. Shukhov Belgorod State Technological University, Belgorod, Russia.

[2] Here and below, unless otherwise stated, the mass content.

TABLE 1.

Glass*	Content, %													
	SiO_2		Al_2O_3		CaO		MgO		Na_2O		P_2O_5		K_2O,* mass	Fe_2O_3,* mass
	molar	mass	molar	mass	molar	mass	molar	mass	molar	mass	molar	mass		
T-1	73.5	73.32	1.5	2.54	9.0	8.38	2.0	1.33	14.0	14.43	0	0	–	–
	–	73.74*	–	2.26*	–	8.20*	–	1.39*	–	13.85*	–	–	0.19*	0.020*
T-2	73.2	72.72	1.5	2.53	9.0	8.34	2.0	1.32	14.0	14.37	0.3	0.71	–	–
	–	74.45*	–	2.15*	–	8.25*	–	0.78*	–	13.10*	–	0.78*	0.12*	0.023*
T-3	72.9	72.13	1.5	2.52	9.0	8.31	2.0	1.32	14.0	14.31	0.6	1.40	–	–
	–	72.28*	–	2.00*	–	8.30*	–	1.10*	–	14.23*	–	1.52*	0.19*	0.030*
T-4	72.6	71.54	1.5	2.51	9.0	8.28	2.0	1.31	14.0	14.26	0.9	2.10	–	–
T-5	72.3	70.96	1.5	2.50	9.0	8.24	2.0	1.31	14.0	14.20	1.2	2.79	–	–
T-6	72.0	70.38	1.5	2.49	9.0	8.21	2.0	1.30	14.0	14.14	1.5	3.47	–	–
	–	71.14*	–	2.09*	–	7.60*	–	1.49*	–	13.95*	–	3.25*	0.12*	0.014*

* The chemical analysis of the glasses was performed at the Central Plant Laboratory of Dmitrovsteklo JSC; the P_2O_5 content was determined at the Analytical Certification Test Center at the N. M. Fedorov All-Russia Scientific-Research Institute of Mineral Resources.

A topological model of silicophosphate glasses, which could be used to construct a logical interpretation of the concentration dependences of their properties, has still not been constructed. Concrete information about the structure of these glasses can be obtained by studying the dilatometric properties. The authors of [8] note that in the system $SiO_2 – P_2O_5$ a maximum is present in the curve of the temperature dependence of vitrification and kinks occur in the CLTE curves of glass at a temperature below the vitrification temperature T_g and also in the density with 12 – 17% P_2O_5. They explain this by a change in the structural position of phosphorus in the silicon – oxygen matrix, due to the formation of energetically more favorable structural fragments.

In our work we investigated the dilatometric properties of silicate glasses containing added amounts of P_2O_5, which are of practical significance, and attempted to give a structural interpretation of the concentration dependences of the properties of these glasses.

In the opinion of the authors of [7], the CLTE of glasses in the solid state reflects only the transition to a more polymerized structure. There is also a correlation between the CLTE and the strength of the field of the modifying cation. The values of the vitrification temperature characterize the structural strength of the glass on the average, and the concentration dependences of the vitrification temperature make it possible to estimate the strength of the bonds between the structural units participating in the network of the glass.

A more informative parameter is the structural CLTE α_s determined as the difference between the equilibrium α_e and instantaneous α_g thermal expansion coefficients of the glass:

$$\alpha_s = \alpha_e - \alpha_g .$$

Here α_g is calculated in a conditionally chosen temperature interval below the interval of vitrification — from T_1 to (T_1 – 50 K), where T_1 is the lower limit of the vitrification interval.

The equilibrium CLTE was determined in an interval of temperatures close to T_g and T_f. It characterizes the state of metastable equilibrium. The structural CLTE reflects the change in the specific volume of glass as a result of the temperature changes in the structure under the conditions of a metastable equilibrium — changes of the coordination of the ions, formation and decay of structural complexes (rings, layers, chains), changes of the ratio between the number of bridge and non-bridge oxygen atoms. The most complete information can be obtained by determining simultaneously all three dilatometric properties of glasses. Additional information about structure can also be obtained by studying the concentration dependences of the density and microhardness, which reflect the degree of polymerization and the strength of the bonds in the glass-forming framework.

Sodium-calcium-alumosilicate glasses, simulating the commercial compositions of container glass, with a lower amount of magnesium oxide and containing variable amounts of P_2O_5 replacing SiO_2 were synthesized for these investigations. The chemical compositions of the experimental glasses (according to synthesis and analysis) are presented in Table 1. The chemical compositions of the experimental glasses T-1, T-2, T-3, and T-6 were determined analytically by the standard photometric weighing method. This method is based on the capability of phosphorus to form color complexes with molybdenum compounds. Comparing these data with calculations shows satisfactory agreement, especially for P_2O_5 content.

The glasses were founded from pure and analytically pure raw materials, and phosphorus oxide was introduced by hydrated sodium orthophosphate $Na_3PO_4 \cdot 12H_2O$. Founding was conducted in an electric furnace with silite heaters at

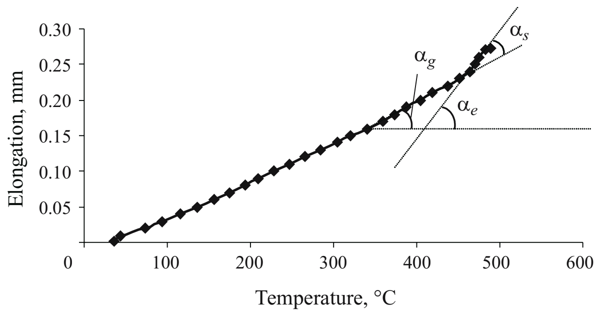

Fig. 2. Temperature curve of the expansion of the glass T-1.

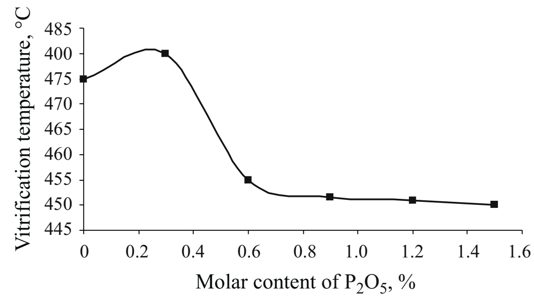

Fig. 4. The vitrification temperature versus P_2O_5 content.

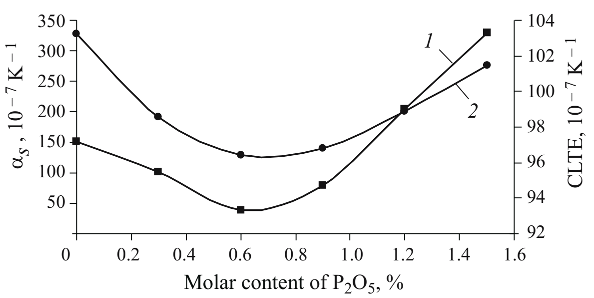

Fig. 3. Dilatometric properties of the synthesized glasses: *1*) CLTE in the temperature interval 20 – 200°C; *2*) structural CLTE α_s.

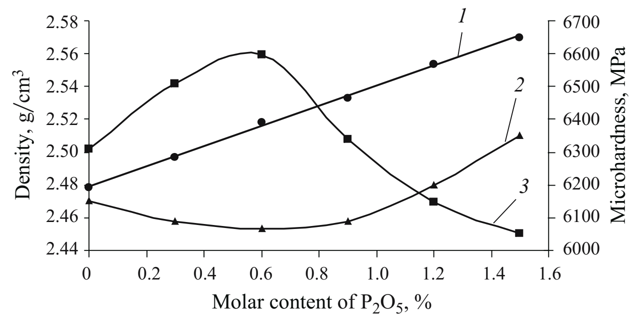

Fig. 5. Structure-sensitive properties of the synthesized glasses: *1*) density calculated by the additivity method; *2*) experimental density; *3*) microhardness.

1400°C in corundum crucibles. The glass was produced by founding and annealed in a laboratory muffle furnace at 600°C.

Additions of phosphorus as a whole did not degrade the founding and production properties of the glasses. All synthesized compositions were x-ray amorphous and structurally uniform, with the exception of the composition T-6, in which opalescence due to liquation phase separation was observed. The x-ray amorphous structure of the glasses was checked on a DRON-3,0M x-ray diffractometer (CuK_α radiation, Ni filter).

The dilatometric properties of the glasses were studied on a DKV-4 quartz dilatometer with constant heating at the rate 3 K/min. The CLTE of solid glass was determined in the dilatometric measurements in the temperature interval 20 – 200°C and the region below α_g and above α_e the vitrification interval. The structural CLTE α_s was calculated from the difference $\alpha_e - \alpha_g$. Figure 2 displays the dilatometric curve of the glass T-1, which illustrates the scheme used to calculate α_s. The determination error did not exceed $\pm 1 \times 10^{-7}$ K^{-1} below and $\pm 5 \times 10^{-7}$ K^{-1} above the vitrification interval, and the vitrification temperature was determined to within ± 5 K.

The density and microhardness were investigated as the structure-sensitive properties. The density of the glasses was measured by hydrostatic weighing in distilled water at 20°C to within ± 0.005 g/cm^3. The microhardness was determined by the Vickers method using a PMT-3 apparatus; the average value of 10 measurements under a 0.186 N (200 gf) load was calculated.

The curve *1* in Fig. 3 shows the variation of the CLTE of glass in the solid state as a function of the P_2O_5 concentration; curve *2* shows the structural CLTE. Both curves have a distinct extremal character: a minimum is observed at the content of 0.6% P_2O_5. A maximum is observed on the curve of the vitrification temperature versus the P_2O_5 content. This maximum is shifted to lower P_2O_5 content — 0.3% or less.

It is interesting to compare the concentration dependences of the experimental glasses with other structure-sensitive properties — density and microhardness (Fig. 5). An extremal character of the dependences is also observed here. The lowest value of the experimental density and the highest value of the microhardness are observed for 0.6% P_2O_5. When the content of P_2O_5, which replaces SiO_2 in glasses, is increased above this value, the density increases and the microhardness decreases.

The difference between the experimental density curve and the density curve obtained by Appen's method, in which the dependence is essentially linear with a constant positive slope, due to the high molar mass of P_2O_5 (142) as compared with SiO_2 (60) is interesting. The difference observed indicates unequivocally the structural changes occurring in a silicate glass when P_2O_5 is added.

Following the regularities established by the authors of [9, 10], it can be asserted that additions of 0.3 – 0.6% P_2O_5 in the silicate glasses studied increase the polymerization and

strength of the structural framework. It can be assumed that in these glasses with a high content of modifiers the concentration of non-bridge oxygen decreases as result of the formation of phosphorus – oxygen anionic motifs and their incorporation into the silica glass-forming framework. However, this cannot fully explain such large differences of the structural CLTE and vitrification temperature. In this case P_2O_5 acts as a binder which "cements" the defective silica glass-forming framework.

The decrease of CLTE of glass in the solid state and the increase of microhardness which are observed when small amounts of P_2O_5 are added to the glass are of practical value. They can be used to develop new compositions of container glass with improved functional properties.

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